

LCA Methodology

A Statistical Approach for Estimation of Process Flow Data from Production of Chemicals of Fossil Origin

Lisbeth Dahllöf¹ and Bengt Steen^{2*}

¹ Volvo Technology Corporation, Environment and Chemistry, 405 08 Gothenburg, Sweden

² Center for Environmental Assessment of Product and Material Systems (CPM) Environmental Systems Analysis, Chalmers University of Technology, 412 96 Gothenburg, Sweden

* Corresponding author (bengt.steen@esa.chalmers.se)

DOI: <http://dx.doi.org/10.1065/lca2005.12.241>

Abstract

Goal, Scope and Background. The life cycles of many products including textiles contain chemicals for which process flow data are not known or are too time consuming to collect. Although each chemical may not contribute significantly to the LCA results of the product, which might justify excluding them, but together their contribution could be significant. Similarly, rough estimates of the process flows for the production of a single chemical may be very uncertain and considered meaningless, while the estimates of the cumulative data of process flows for several chemicals may be less uncertain and be a meaningful contribution to the quality of the LCA results. There are methods for estimation of process flows for different types of products, with varying demands regarding input data and time and with varying accuracy of the results. This work contributes to the available methods, focusing on simple estimations for production of chemical substances. The goal was to create a fast method for estimation of emissions, resource and energy flows (process flows) for the production of chemicals, based on easily available data on the properties of the chemicals. The process flows investigated were limited to those normally associated with process industries and contributing most to depletion of resources, to global warming, acidification, eutrophication and photochemical ozone production, i.e. use of energy, crude oil, coal, natural gas, uranium in ore and emissions of CO₂, SO_x, NO_x, NMVOC, methane, BOD, COD and total N. Toxic substances were excluded, since toxic emissions are substance specific and cannot be included in a generalization.

Method. Available data for the process flows for the production of chemicals of mainly fossil origin were correlated to properties of chemicals such as amount of carbon in the molecule, heat of formation and average number of chemical reaction steps in the production. The production procedures were found in readily available literature. Up to about six reaction steps were evaluated in the correlation study. The variations in the process flows among the chemicals studied were calculated.

Results and Discussion. There were weak correlations between average number of chemical reaction steps in the production and energy use, COD measured in water emissions, and SO_x and NO_x emissions to air. For the remaining properties of chemicals and process flows, there were only weak correlations for share of double bonding in the molecule if only molecules containing double bondings were included.

Conclusions. The precision in estimation of the process flows increases non-significantly when adding information on the number of reaction steps or share of double bonding for chemicals containing double bonding is added.

Recommendations and Outlook. It seems reasonable to start with a simple grouping method to estimate the process flows for the production of a chemical of fossil origin. Further investigations might investigate whether there is a correlation between process flows and the costs of chemicals, and further study the correlations between process flows and share of double bonding for chemicals containing double bondings.

Keywords: Average number of reaction steps; environmental impacts; estimation methods; process flow; properties of chemicals; standard deviation of estimates

Introduction

Life Cycle Assessment (LCA) studies are often time consuming and involve auxiliary materials, such as chemicals used in the manufacturing of textiles. The life cycle of a cotton fabric can, for instance, contain more than 50 different chemicals (Dahllöf 2004). The LCA practitioner sometimes excludes the production of the chemicals, on the assumption that each of them is used in such a small quantity that it does not contribute tangibly to the environmental impact. The problem is that many chemicals used in small amounts can have a significant cumulative environmental impact. Therefore there is a need for rules of thumb regarding estimation of environmental impacts from production of chemicals.

The problem of data gaps for production of chemicals is common in screening LCAs and some attempts have been made to solve the problem. Bretz and Frankhauser (1996) have described their LCA system ECOSYS, used at CIBA's Textile Dyes and Chemicals divisions. They have developed a generic set of data for common unit processes, like preparation and incineration of fuels, waste treatment and chemical standard operations. Their program automatically checks the flow of fuels, waste etc. and adds emissions and resource flow figures if missing. ECOSYS facilitates LCA studies for CIBA, and lends itself to sensitivity analysis. Since a lot of the data are, however, not made available for practitioners outside CIBA, the LCA system is of limited value outside the company. No verification of the method was reported.

Jiménez-González et al. (2000a) had a similar approach. They created gate-to-gate modules using 'chemical engineering process design techniques'. The methodology for creating the modules is: 1) search and selection of the process, 2) definition of the process (e.g. description of chemical reactions, identification of conditions, determination of reaction and separation efficiencies), 3) mass balance calculations and 4) energy calculations. The method was tested for ammonia production. Best forecasting power was found for energy use when comparing with 4 other data sources. Jiménez-González et al. (2000b) have also made an investigation regarding the extent to which process flow data differ between data sources for refinery products: 'The variability of estimated emissions to the atmosphere is approximately 50–150%, while variability in aqueous discharges is higher, approaching 1000%'.

In the examples above, no new methodology on how to generalize calculations of process flow data from chemical production could be found. Geisler et al. (2004), however, have developed a new methodology by creating a generic input-output scheme and equations for calculation. The scheme includes reactions and workup. Inputs are substrates, solvents, steam, electricity, cooling water and nitrogen, and outputs are materials to next process steps, air emissions, wastewater to a wastewater treatment plant module and waste to an incinerator module. For most process flow data in the estimation procedure created, default values were derived from on-site data on chemical production processes and from heuristics. Where data for the equations were unknown, default values were used. The results were reported as a range, from worst to best case. Although this method requires specific knowledge about what the process steps are, which is not always available to LCA practitioners, it can handle data gaps. The authors showed successful partial validation for primary energy demand and human toxicity potential for a specialty chemical.

One simple method for estimating combined characterized and weighted process flow data for materials is found in Sun et al. (2003). They grouped materials according to their chemical and physical properties and collected process flow data for their production in order to give a rule of thumb for the estimation of the environmental impact of the production of materials. The data collected varied depending on product group, but they were all air emissions and resource use. The authors tested the method on a case where characterized and weighted process flow data for the material production of two different coffee machines was searched for. The results were found to deviate up to 26% when data for material groups instead of single materials was used. The principle of grouping could also be applied to chemical substances.

1 Aim and Method

The aim of our study was to develop new, more time saving methods than the method described by Geisler et al. (2004), methods more sophisticated than grouping, to estimate process flow data for production of chemicals. Our intention was that it should not take more than about half an hour to estimate the values for each chemical. The method is intended to be used when there are many chemicals in a life cycle with unknown data for impacting on process flows

from their production. Large amounts of missing data may cause problems in setting the system boundaries, identifying hotspots in the life cycles, or making environmental comparisons between different life cycles.

The objective was to find correlations between process flow data and some easily available data for properties of chemicals of mainly fossil origin.

The properties of the chemicals tested for the correlations were:

- amount of carbon,
- amount of double bonding,
- amount of triple bonding,
- share of double bonding (weight of carbon in the double bondings divided by total weight),
- share of aromatics (weight of carbon in the aromatic rings divided by total weight),
- share nitrogen (weight of nitrogen divided by total weight),
- Gibbs free energy of formation,
- enthalpy of formation and
- average number of chemical reaction steps (number of reaction steps).

The main source from which we retrieved information regarding Gibbs free energy and the enthalpy of formation was Lange's Handbook of Chemistry (Dean 1992), but also to some extent Ullmann's Encyclopedia of Industrial Chemistry (2001) or Kirk-Othmer Encyclopedia of Chemical Technology (Kirk & Othmer 1991).

Reaction steps were calculated from information about the production of the chemical in either Ullmann's Encyclopedia of Industrial Chemistry (2001) or Kirk-Othmer Encyclopedia of Chemical Technology (Kirk & Othmer 1991), which are available on-line. For many of the chemicals there is more than one process described. This gives rise to problems in choosing which process to base the calculations on. Moreover the information about the production is sometimes scarce, as in the case of LAS, a surfactant. However, the chemical reactions are often described. An alternative to using pure reaction steps as an independent property of the chemical would have been to include other energy-demanding process steps such as distillation columns, etc., but this would make our method similar to that of Geisler et al. (2004) in terms of complexity, and the calculations would require considerably more than half an hour per chemical. Therefore, in this study, we focused on the average number of reaction steps. This means in practice that physical operations such as distillation were assumed to have a constant relation to the chemical reaction(s). If the process tree had several branches, the number of reaction steps was the stoichiometric weighted average of all branches. For an example of a calculation (Fig. 1).

The reaction product H_2O was not taken into account, since it was assumed not to be used. Since the literature was unclear about which form the oxygen was added, it was assumed that the oxygen was added as oxygen gas and not as a component in air.

The rules for the calculations were:

- Water and air were assumed to need 0 reaction steps, since they are readily available in nature.
- Crude oil, natural gas, nitrogen gas, oxygen gas, NaCl, S are extracted from nature, and so one reaction step

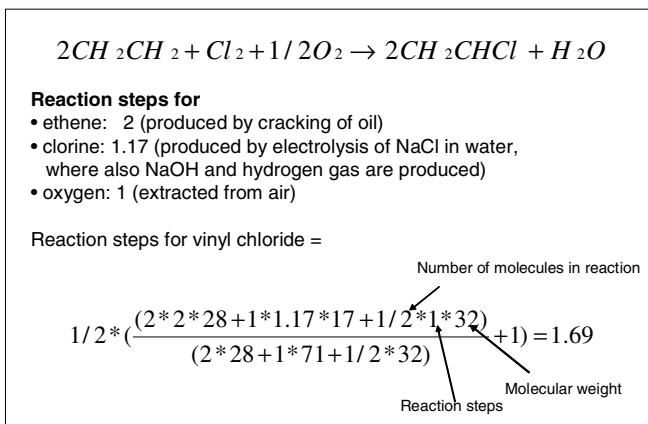


Fig. 1: Calculation of number of reaction steps for vinyl chloride

was assumed. Extraction from nature is the only case where the term 'reaction step' is used for something other than a reaction.

- No purification process was calculated as a reaction step.
- No solvents or catalysts were included in the calculations. To include them would improve the estimation, but would make it more complicated.
- If there was more than one possible process with different chemical reactions, but if one was dominant (more than 70% of the production of the chemical) only the dominant process reactions were calculated.
- If it was not known how common the different process types were, calculations for reaction steps were done for

each process and an average value for reaction steps thereafter calculated.

- Reactions that only create intermediates were not calculated. This was to avoid having several reaction steps from a reaction mechanism with several short-lived intermediates within the same process step.
- If water is used in the reaction, it was included in the calculation if it becomes a part, or to some extent becomes a part, of the product.
- If oxygen is used in the reaction, but it is not known if air or pure oxygen gas is used, pure oxygen gas was assumed.
- If the oxygen gas used in the reaction only becomes a part of the produced water, which is not used, the oxygen is still included in the calculation, but if the oxygen comes from air it was not calculated with.

The process flows investigated were limited to those normally associated with process industries and which belonged to those most contributing to depletion of resources, global warming, acidification, eutrophication and photochemical ozone production. These were use of energy, crude oil, coal, natural gas, and emissions of CO_2 , SO_x , NO_x , NMVOC, methane, BOD, COD and total N (N_{tot}). U in ore was excluded, since the APME studies (APME 2004) did not report the U in ore values. Toxic substances were also excluded, as we did not expect to find any correlation between production steps and toxicity.

2 Results and Discussion

The chemicals used for the calculations are found in Table 1 together with the calculation results of reaction steps.

Table 1: Substances included in the inventory model for chemical production together with the calculation results of reaction steps. These chemicals were chosen because we had inventory data for their production

Chemical (of mainly fossil origin)	Data source	Reaction steps ¹
Acetone (H^2, G^3)	APME (2004, 1996 ⁴)	1.86
Acetone cyanohydrin	APME (2004, 1992–1993 ⁴)	2.65
Acrylonitrile	APME (2004, 1990–1996 ⁴)	2.42
AE ⁵	Dall'Acqua et al. (1999)	3.04
Benzene (H^2, G^3)	APME (2004, 1989–1995 ⁴)	2.46
Bisphenol A	SPIN (1991 ⁶)	3.68
Butadiene	APME (2004, 2003 ⁷)	2.00
Butenes (H^2, G^3)	APME (2004, 1989–1995 ⁴)	2.00
Carbon black	Frischknecht et al. (1996 ⁶)	2.00
Ethylene (H^2, G^3)	APME (2004, 2003 ⁷)	2.00
Ethylene glycol	Frischknecht et al. (1996 ⁶)	3.13
Formaldehyde (H^2, G^3)	Frischknecht et al. (1996 ⁶)	3.16
Hydrogen cyanide (H^2, G^3)	APME (2004, 1992–1993 ⁴)	1.98
LAS ⁵	Dall'Acqua et al. (1999)	4.76
MDI ⁵ average	Average of APME (2004, 1995–1996 ⁴) and APME/ISOPA (1996 ⁶)	5.33
MTBE ⁵	Frischknecht et al. (1996 ⁶)	3.06
Pentane (H^2, G^3)	APME (2004, 1990–1996 ⁴)	1.00
Phenol (H^2, G^3)	Frischknecht et al. (1996 ⁶)	2.93
Propylene (H^2, G^3)	Frischknecht et al. (1996 ⁶)	2.00
PTA ⁵	APME (2004, 2002 ⁷)	2.64
Styrene (H^2, G^3)	APME (2004, 1990–1994 ⁴)	4.60
TDI ⁵ average	Average of APME (2004, 1995–1996 ⁴) and Frischknecht et al. (1996 ⁶)	3.38
Toluene (H^2, G^3)	APME (2004, 1990–1996 ⁴)	2.00
Vinyl chloride	Average of APME (2004, 1992–1995 ⁴) and Frischknecht et al. (1996 ⁶)	1.69
Xylene average (H^2, G^3)	Average of APME (2004, 1990–1996 ⁴) and Frischknecht et al. (1996 ⁶)	3.00

¹ Reaction steps = stoichiometric weighted average number of reaction steps; ² H = data found for enthalpy of formation; ³ G = data found for Gibbs free energy of formation; ⁴ Years for which data were collected; ⁵ For abbreviations, see glossary; ⁶ From SimaPro 5.1 Demo version (2002); ⁷ Revision year

Due to insufficient data in the Ullmann and Kirk-Othmer encyclopedia, the following chemicals were excluded:

- Esterquat of tallow oil¹
- Esterquat of coconut oil/palm kernel oil¹
- CMC¹
- SAS¹

R, the linear regression coefficient, was chosen to identify and rank relations. Linear methods were preferred to nonlinear methods because emissions from different process steps were expected to be uncorrelated to each other. The correlation was weak for all properties of chemicals. The correlations studies are summarized in Table 2.

The best correlation was found for air emissions of NMVOC and share of nitrogen in the molecule for chemicals containing nitrogen, but there were only four chemicals in the calculation, which makes the value of the regression very low. The value of the regression is also low for share of aromatics although R may be high, owing to the limited amounts of chemicals included. The property 'share of double bonding', included however 13 chemicals in the calculations, and some correlations were found for some properties. The best correlations were found for the properties number of reaction steps and share of double bonding with only chemicals containing double bonding. In Fig. 2 the best correlation for the property number of reaction steps is shown, and in Fig. 3, the best correlation for the property share of double bonding with only chemicals containing double bonding is shown.

The standard error for the regression in Fig. 2 is 14.3 MJ/kg (regression of energy use for the production of 1 kg of a chemical and the estimated average number of reaction steps

¹ For abbreviation, see Glossary.

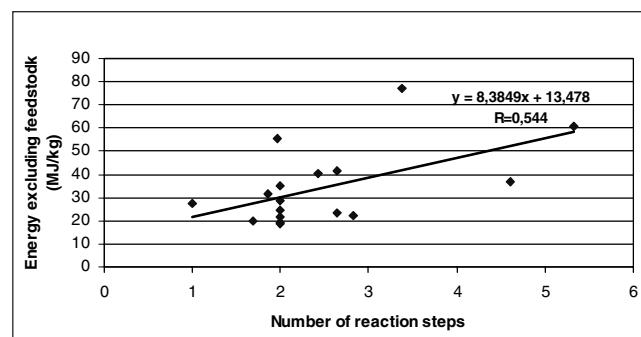


Fig. 2: Correlation between energy use for the production of 1 kg of a chemical and the estimated average number of reaction steps for chemicals of mainly fossil origin. Data for the energy use were only found in the APME studies

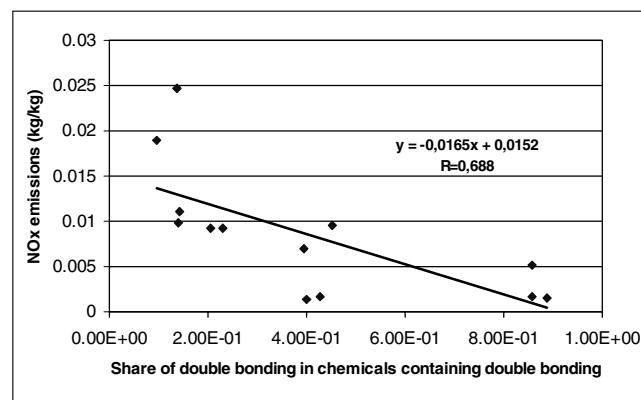


Fig. 3: The correlation between NO_x emissions from the production of 1 kg of chemical and share of double bonding in chemicals containing double bonding

Table 2: Overview of the correlation results for chemicals of mainly fossil origin

Property of chemical	Process flow			Use of resources		Air emissions				Discharges to water			Energy
	Natural gas	Crude oil	Coal	CO ₂	SO _x	NO _x	NMVOC	CH ₄	BOD	COD	Ntot	Energy without feedstock	
Average number of reaction steps					+	+					+		+
Share of aromatics		(+) ¹	(+) ¹							(+) ¹			(+) ¹
Share of double bonding	(+) ²			(+) ²			(+) ²						
Share of nitrogen	+	(+) ³	(+) ³	+	(+) ³	(+) ³	+	+					
Amount of carbon											+		
Amount of double bonding													
Amount of triple bonding												+	
Gibbs free energy of formation													
Enthalpy of formation												+	+

¹ 7 data points in the calculations for chemicals containing aromatics only

² 13 data points in the calculations for chemicals containing double bonding only

³ 4 data points in the calculations for chemicals containing nitrogen only

+= some correlation found (correlation coefficient ≥ 0.40)

+ in brackets are results for a limited group of chemicals, i.e., those containing double bonding, aromatics or nitrogen respectively. Share of "X" means weight of carbon in the double bonding(s) or aromatic ring(s), or weight of nitrogen respectively divided by total weight of chemical

24 to 25 chemical substances included in the calculations

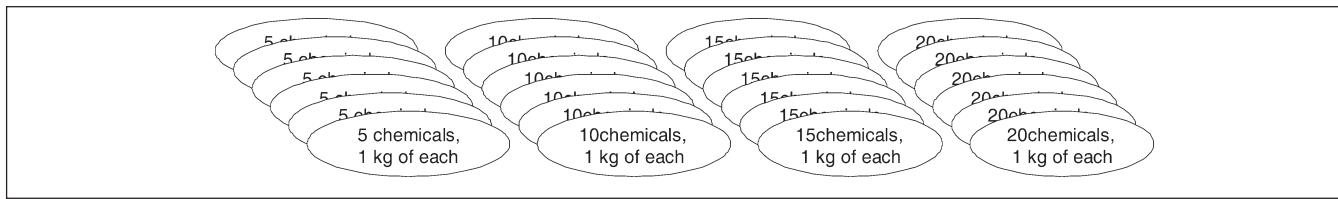


Fig. 4: Illustration of the choice of chemicals for the precision test

for chemicals of mainly fossil origin) The standard deviation of estimate (s) for the average value is 16.5. Thus, there is no significant gain in calculating the reaction steps for the chemical and using a regression curve to calculate the energy use requirement for the chemical production.

For the share of double bonding in chemicals there was a slightly negative correlation with NO_x emissions. It is difficult to explain why it should be negative (a positive correlation could have indicated a more elaborate synthesis), which makes the estimation method questionable. The fact that it is only applicable to chemicals containing double bonding is also a limitation.

A significant increase in precision is however achieved when estimated process flow data are summarized for several chemicals. This is illustrated in the following test:

6 sets of chemicals were chosen randomly from Table 1, containing 5, 10, 15, 20 chemicals respectively (Fig. 4). Thus, the same chemical could appear within the same data set more than once.

The total NO_x emissions from production were calculated using estimated average data as one alternative and literature data as the other.

The deviations from literature data for the average estimated NO_x emissions are shown in Fig. 5 as calculated using Eq. (1):

$$\text{Deviation (\%)} = \left| 1 - \frac{\text{sum}_{\text{av}}}{\text{sum}_{\text{litt.}}} \right| * 100 \quad (1)$$

where

Deviation (%) = deviation in % from the summarized literature values.

$\text{sum}_{\text{av}} =$ the summarized value for a type of process flow, such as NO_x emissions, calculated using the average value for the data set.

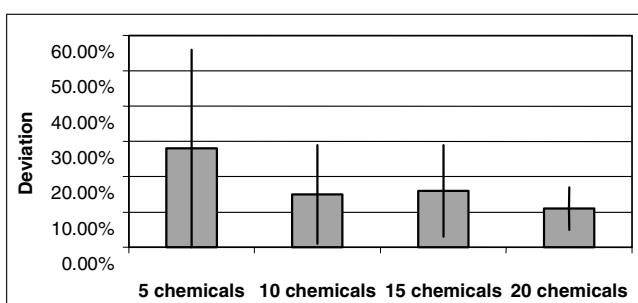


Fig. 5: Comparison between literature and average data for the calculation of NO_x emissions for hypothetical products containing 5, 10, 15 and 20 chemicals

$\text{sum}_{\text{litt.}} =$ the summarized value for a type of process flow, such as NO_x emissions, calculated from the literature.

Fig. 5 illustrates the increase in precision in the estimated emissions of NO_x per kg of chemicals with increasing numbers of chemicals in the calculations of total NO_x emissions for all the chemicals in the study as calculated with (1). Thus, we can see that low precision estimation methods could be justified if an LCA study contains many chemicals in a defined group of chemicals with unknown production data.

The cumulative uncertainty of the estimated emissions of several chemicals can be estimated using the calculation of the population standard deviation of estimate (σ), see the Eq. (2):

$$\sigma = \frac{s}{n} \sqrt{\sum_{i=1}^n C_i^2} \quad (2)$$

C_i = weight of chemical i (in kg)

s = sample standard deviation of estimate (/kg chemical)

σ = population standard deviation of estimate (/kg)

n = number of chemicals in the calculation

If it is assumed that the process flows are independent between the reaction steps of a process, the regression curves found in Fig. 2 and 3 may be predicted as linear and as having a standard deviation that increases with the square root of the number of reaction steps. This seems to be the case in Fig. 2 and 3.

3 Conclusions

We did not find a significant improvement in estimating process flows from the production of chemicals of mainly fossil origin, as compared with the method of grouping. The 'average number of reaction steps' showed weak correlations with energy use, SO_x and NO_x emissions to air, and COD measured in water emissions. The 'share of double bonding in the molecule' showed weak correlations with energy, natural gas and coal use, air emissions of NO_x , SO_x , CO_2 and NMVOC, and BOD measured in water emissions, if only molecules containing double bonding(s) were included in the calculations. The value of the method is therefore limited, especially for single substances, but if the alternative is to set production data to 0, it could be useful in screening LCAs. When estimated process flow data from several chemicals are summarized, however, the standard deviation per kg of chemical decreases.

4 Recommendations and Outlook

Estimated process flow data for production of chemicals are particularly useful when an LCA study contains several chemical substances with unknown data. Using a statistical approach to the LCA study, these estimated values together with their standard deviation of estimate can be incorporated into an LCA study. In the ideal case, the standard deviations of estimates for all process flows and characterization factors are known, and the uncertainty of the LCA results can be calculated. The need for quality governs the choice of estimation method.

If a reasonable explanation for the correlation of elementary flows and share of double bonding for chemicals containing double bonding could be found, it would be of interest to further investigate the correlations.

It would be interesting to test production costs as a property of chemical, since it is likely that a higher price indicates a complex production process. Our experience is, however, that information on such costs is difficult to obtain.

For chemicals of mainly non-fossil origin, regression trials could also be performed. However, our preliminary tests on the parameters number of reaction steps, Gibbs free energy of formation, and enthalpy of formation, showed even weaker correlations than for chemicals of mainly fossil origin. Moreover we found it more difficult to find sufficient information regarding production reactions.

Glossary

Chemical names	
AE	Alcohol ethoxylate (here with 7 EO chains from petrochemical raw materials, nonionic surfactant)
CMC	Carboxymethyl cellulose
DSBP	Distyrylbiphenyl type of fluorescent whitening agent
Esterquat coconut oil/palm kernel oil	$(N(CH_3)(CH_2CH_2OCOR)_2(CH_2CH_2OH)) + (CH_3SO_4^-)$, kationic surfactant
Esterquat tallow oil	$(N(CH_3)(CH_2CH_2OCOR)_2(CH_2CH_2OH)) + (CH_3SO_4^-)$, kationic surfactant
LAS	Linear alkylbenzene sulphonate from petrochemical raw materials, anionic surfactant
MDI	Diphenylmethane-diisocyanate
MTBE	Methyl Tertiary Butyl Ether
PTA	Pure terephthalic acid
SAS	Secondary alkane sulphonate, anionic surfactant from straight chain paraffins
Soap	From natural oils (coconut oil, palm oil)
TDI	Toluene-diisocyanate

Acknowledgements. We thank the Centre for Environmental Assessment of Product and Material System, CPM, in Gothenburg, Sweden, for funding our research.

References

APME (2004): Eco-Profiles of the European plastics industry. Association of Plastics Manufacturers (PlasticsEurope), Boustead I (ed), retrieved from the Internet March, <<http://www.apme.org>>, Brussels

APME/ISOPA (1996): Ecoprofiles of the European plastics industry. Report 9, Polyurethane precursors (TDI, MDI, Polyols) <<http://www.isopa.org>>

Bretz R, Frankhauser P (1996): Screening LCA for Large Numbers of Products: Estimation Tools to Fill Data Gaps. *Int J LCA* 1 (3) 139–146

Dahllöf L (2004): Methodological Issues in the LCA Procedure for the Textile Sector – A case study concerning fabric for a sofa. Environmental Systems Analysis, Chalmers University of Technology, ESA– Report 2004:7, <www.esa.chalmers.se>, <http://www.esa.chalmers.se/Publications/PDF-files/TR_ESAReport20047.pdf>, Göteborg, Sweden

Dall'Acqua S, Fawer M, Fritsch R, Allenspach C (1999): Life Cycle Inventories for the Production of Detergent Ingredients. Swiss Federal Laboratories for Materials Testing and Research (EMPA) Report No 244, St. Gallen, Switzerland

Dean JA (ed) (1992): Lange's Handbook of Chemistry. 14th edition, McGraw-Hill, Inc, New York

Frischknecht et al. (1996): Öko-inventare von Energiesystemen. ETH-ESU, 3rd ed <<http://www.energieforschung.ch>>

Geisler G, Hofstetter TB, Hungerbühler K (2004): Production of Fine and Speciality Chemicals: Procedure for the Estimation of LCIs. *Int J LCA* 9 (2) 101–113

Jiménez-González C, Kim S, Overcash MR (2000a): Methodology for Developing Gate-to-Gate Life Cycle Inventory Information. *Int J LCA* 5 (3) 153–159

Jiménez-González C, Overcash M (2000b): Life Cycle Inventory of Refinery Products: Review and Comparison of Commercially Available Databases. *Environmental Science & Technology* 34, 4789–4796

Kirk RE, Othmer DE (eds) (1991): Encyclopedia of Chemical Technology. John Wiley & Sons, New York

SimaPro 5.1 Demo version (2002): Pré Consultants bv, <<http://www.pre.nl>>

Spin (1991): Polycarbonate, from SimaPro 5.1 Demo version (2002)

Sun M, Rydh CJ, Kaebernick H (2003): Material Grouping for Simplified Product Life Cycle Assessment. *Journal of Sustainable Product Design* 3, 45–58

Ullmann's Encyclopedia of Industrial Chemistry (2001): John Wiley & Sons, New York, 6th ed

Received: November 25th, 2004

Accepted: December 12th, 2005

OnlineFirst: December 13th, 2005